



Dynamic fabric phase sorptive extraction for a group of pharmaceuticals and personal care products from environmental waters[☆]



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ABSTRACT

This paper describes for the first time the use of a new extraction technique, based on fabric phase sorptive extraction (FPSE). This new mode proposes the extraction of the analytes in dynamic mode in order to reduce the extraction time. Dynamic fabric phase sorptive extraction (DFPSE) followed by liquid chromatography-tandem mass spectrometry was evaluated for the extraction of a group of pharmaceuticals and personal care products (PPCPs) from environmental water samples. Different parameters affecting the extraction were optimized and best conditions were achieved when 50 mL of sample at pH 3 was passed through 3 disks and analytes retained were eluted with 10 mL of ethyl acetate. The recoveries were higher than 60% for most of compounds with the exception of the most polar ones (between 8% and 38%). The analytical method was validated with environmental samples such as river water and effluent and influent wastewater, and good performance was obtained. The analysis of samples revealed the presence of some PPCPs at low ng L⁻¹ concentrations.

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1. Introduction

Pharmaceuticals and personal care products (PPCPs) are extensively used in our day-to-day life and, after their consumption, they often enter into the environment, mainly from household water because of their ability to pass through the wastewater treatment plants. Their presence may affect human and aquatic life, as they are known to be hazardous and may be accumulated in various environmental compartments due to their continuous release into the environment. Consequently, these compounds are frequently found in waste, surface and even ground water [1–5]. Thus, they are considered to be contaminants of emerging concern.

Due to the growing interest in determining contaminants at low concentration levels in complex matrices, many different extrac-

tion techniques have been developed. For liquid samples in the last years, solid-phase extraction (SPE) has become the technique of choice [6–8], although some other techniques have been successfully applied, such as solid-phase microextraction (SPME) [9,10] and stir bar sorptive extraction (SBSE) [11,12], among others. However, the most important drawbacks of these techniques [13–15] are the low sorbent present in the fibres of SPME, and the limited number of available sorbent type and slow analyte diffusion rate through polymeric coating in SBSE.

A novel sorptive extraction technique, fabric phase sorptive extraction (FPSE), was recently introduced by Kabir and Furton [16]. This technique consists of the use of a flexible fabric substrate surface coated with different polymers/functional moieties using sol-gel technology so that high primary contact surface area is available for extraction. These unique sorbent chemistries have been developed to cover wide range of analyte polarities and include sol-gel Carbowax 20M [17], sol-gel poly(tetrahydrofuran) [18], sol-gel poly(dimethyldiphenylsiloxane) [19,20], among others. The sol-gel coated FPSE medium (25 × 20 mm²) can be directly introduced into the sample for the analyte extraction and, once equilibrium is reached, the analytes retained on the extraction

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medium can be back-extracted using a small volume of organic solvent [21].

To date, FPSE has been applied to extract several analytes from different samples, such as benzotriazole UV stabilizers in sewage samples [22], alkyl phenols in aqueous and soil samples [23], benzodiazepines in blood samples [24], estrogens in urine and environmental water samples [18], polar antibiotic in raw milk [25], non-steroidal anti-inflammatory drugs [19] and triazine herbicides in environmental water samples [20]. Our research group evaluated FPSE for the extraction of a group of PPCPs followed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) with satisfactory results [17]. However, the main drawback of FPSE was the extraction time (up to four hours) required to reach the extraction equilibrium. To overcome this long extraction time, a new mode of the FPSE approach is proposed, called dynamic fabric phase sorptive extraction (DFPSE). DFPSE uses 47 mm circular disks of FPSE media coated with sorbent material of different polarities using sol-gel coating technology. In the new extraction mode of FPSE, the sample is percolated through the FPSE disks installed on a filtration assembly. Following the extraction of the target analytes into the FPSE disks, the retained analytes are eluted by passing a volume of the elution solvent through the same assembly. This configuration may decrease the equilibrium time while maintaining the rest of features.

The present work describes for first time the use of the DFPSE technique whose performance efficiency was evaluated using a group of PPCPs in environmental water samples. In this study, different parameters affecting the dynamic extraction mode were optimized and the results were compared with those obtained with static FPSE, where the sol-gel Carbowax 20M coated media were also used [17]. Subsequently, a method was developed based on the new DFPSE mode followed by LC-MS/MS and it was validated for the determination of PPCPs from river and wastewater samples.

2. Materials and methods

2.1. Reagents and standards

Substrates for fabric phase sorptive extraction (FPSE) media (unbleached Muslin, 100% cellulose cotton fabric) were purchased from Jo-Ann Fabric (Miami, FL, USA). Poly(ethylene glycol) (Carbowax 20M) polymers, acetone, dichloromethane, methyltrimethoxysilane (MTMS), trifluoroacetic acid (TFA) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Thermo Fisher Scientific (Milwaukee, WI, USA).

The reagents for the analytical evaluation were: paracetamol (PARA), caffeine (CAFF), antipyrine (APy), propranolol hydrochloride (PROP), methylparaben (MPB), carbamazepine (CBZ), propylparaben (PrPB), 2,4-dihydroxybenzophenone (DHB), benzylparaben (BzPB), 2,2-dihydroxy-4-4-methoxybenzophenone (DHMB), diclofenac (DICLO), 3-benzophenone (BP-3), triclocarban (TCC) and triclosan (TCS) and all of them were purchased from Sigma-Aldrich (Steinheim, Germany). Stock solutions of individual standards were prepared by dissolving each compound in methanol (MeOH) at concentration of 1000 mg L⁻¹. A mixture of standards of all compounds at 50 mg L⁻¹ was prepared in MeOH every month. Working standard solutions were prepared weekly by diluting with mixture of ultrapure water at pH 3 and ACN (80:20, v/v). All the solutions were stored at 4 °C. Ultrapure water was obtained from a water purification system (Veolia Waters, Barcelona, Spain) and the elution solvent was evaporated using the miVac Duo system (Genevac, Ipswich, United Kingdom). HPLC grade MeOH, acetonitrile (ACN) and ethyl acetate (EtOAc) were supplied by Scharlab (Barcelona, Spain). Sodium chloride (NaCl)

and formic acid (HCOOH) (95% purity) were purchased from Sigma-Aldrich.

2.2. Preparation of FPSE media

Preparing the substrate for sol-gel coating, design and preparation of the sol-gel coating solution, applying the sol-gel coating on the pre-treated substrate, conditioning and ageing of the sol-gel coated FPSE media, and the post-coating cleaning of the FPSE media are the sequential steps that are followed to create an inherently porous sol-gel coated permeable FPSE media. A detailed account on every steps mentioned herein are described elsewhere [17]. However, a summary of the entire process is given below. Selection of the suitable FPSE media takes into consideration the hydrophobicity or hydrophilicity of the target analytes. Considering the fact that majority of the selected PPCPs are either highly polar (PARA, CAFF, APy, MPB, CBZ) or moderately polar (PROP, PrPB, DHB, BzPB), a hydrophilic substrate would have been a suitable choice as the substrate may synergistically complement to the overall polarity and the selectivity of the FPSE media. As such, 100% cotton cellulose, being a hydrophilic substrate, was selected as the substrate for sol-gel coating. The cellulose fabric support was treated with NaOH solution to activate surface hydroxide groups, neutralized with dilute HCl, washed with deionized water and dried in an inert atmosphere prior to the sol-gel coating. Due to the good results obtained in previous study [17] using FPSE, a polar polymer Carbowax 20M was selected as the organic polymer from a large number of polymer candidates. Methyltrimethoxysilane (MTMS) was used as the sol-gel precursor in order to prevent from shrinking and cracking of the sol-gel coating often seen when trimethoxysilane or triethoxysilane are used as the sol-gel precursor. In addition to prevent the sol-gel coating from cracking and shrinking, MTMS also exerts London dispersion type of intermolecular interaction *via* methyl functional groups towards the target analytes. TFA was used as the sol-gel catalyst. Formation of a homogeneous sol solution incorporating all the sol solution ingredients is of prime importance to the success of a sol-gel coating. An equimolar mixture of dichloromethane and acetone was needed to prepare homogeneous sol solutions for sol-gel Carbowax 20M coatings. The molar ratio between the sol-gel precursor and Carbowax 20M was kept at 1:0.02. The molar ratio between sol-gel precursor, solvent, catalyst, and water was maintained at 1:3.90:1.31:0.30, respectively.

Sol-gel coating was carried out *via* dip coating technique. The pre-treated substrates were kept submerged in the sol solution for four hours and then sol solution was discarded and the coated fabrics were transferred into a desiccator for conditioning and ageing of the sol-gel coating. The coated FPSE media were then rinsed with a mixture of dichloromethane:acetone (50:50; v/v) under sonication for 30 min to remove unreacted sol solution ingredients as well as other sol-gel reaction intermediates or by-products from the FPSE media. Finally, after drying the FPSE media in an inert environment, they were cut into 47 mm diameter FPSE disks.

2.3. Dynamic fabric phase sorptive extraction

The DFPSE conditions were optimized using sol-gel Carbowax 20M coated FPSE media. Prior to any extraction, the FPSE disks, placed in the filtration assembly, were conditioned and equilibrated by passing 10 mL MeOH followed by 10 mL of ultrapure water, and then dried by applying vacuum. For the extraction, 50 mL of sample (25 mL for influent wastewater) adjusted to pH 3 with HCOOH and containing 10% of NaCl (w/v) were loaded. Then, the sample was left for 10 min in contact with the FPSE disk for the retention of analytes. After 10 min, a vacuum was applied to pass the sample through the FPSE disk completely, and then to dry the FPSE media. The retained analytes were eluted by passing 10 mL of EtOAc

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